Crystallographic and magnetic phase transition in TiMnCl₃

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Abstract. The results of our NMR, EPR and magnetic susceptibility measurements in the paramagnetic state of TiMnCl₃ are reported here. The NMR paramagnetic shift of thallium is found to be small but positive. Mn²⁺ EPR line is exchange narrowed. The susceptibility measurements indicate an antiferromagnetic transition. The heat of crystallographic phase transition ΔH, in TiMnCl₃, has been measured using differential scanning calorimetry. The crystallographic phase transition appears to be first order and ΔH is unusually low viz. 10 cal mole⁻¹. In the case of KMnF₃, ΔH, which is reported here for the first time, is determined to be 2 cal mole⁻¹.

Keywords. Phase transition, antiferromagnetic; differential scanning calorimetry; TiMnCl₃; KMnF₃

1. Introduction

Many ionic compounds of the ABX₃ type crystallise in the perovskite structure in which B ions are situated in the holes created by close packing of AX₃ layers. TiMnCl₃ belongs to this class of compounds. In a recent paper, Melamud et al. (1971) have discussed in detail the similarities in many physical features of TiMnCl₃ and KMnF₃, another member of the ABX₃ perovskite family. Both undergo a cubic→tetragonal crystallographic phase transition, believed to be due to the softening of the Γ₅₅ phonon mode. The magnetic ions (Mn²⁺) in both these compounds are known to order into an antiferromagnetic arrangement (of G-type) below their respective Neel temperatures. Further, the Goldschmidt number for both of these is the same (∼0.88) whereas the commonly encountered number in perovskites is in the range of 0.90—0.93. KMnF₃ has been studied extensively by many different physical techniques such as neutron diffraction (Minkiewicz and Shirane 1969), x-ray diffraction (Minkiewicz et al. 1970), EPR (Gulley et al. 1969), NMR (Shulman and Stuart 1961, Minkiewicz and Nakamura 1966) (of F¹⁹ and Mn⁵⁸), etc. On the other hand, no results of the NMR, EPR, susceptibility and heat of transition measurements are available for TiMnCl₃. In this paper, we present the results of our measurements on TiMnCl₃ and KMnF₃.

2. Preparation

The sample of polycrystalline TiMnCl₃ was made by heating equimolar quantities of TlCl and MnCl₂·4H₂O in a stream of dry Cl₂ gas instead of HCl (Kestigian 1970). An
orange coloured lump was obtained. TlMnCl$_3$ was always handled in a drybox under dry nitrogen. The cell-constants of a single crystal grown from this powder of TlMnCl$_3$ agreed very well with those reported in literature. Chips of single crystal KMnF$_3$ were made available to us by Dr S Mitra. Finely ground powder of a few of these chips was used. A Perkin-Elmer DSC 1B was used for differential scanning calorimetric (DSC) work. For magnetic susceptibility the standard Gouy technique was used. A Varian Associates wide line NMR Spectrometer was used for all NMR measurements. Thallium NMR was observed at 7, 9, 12 and 16 Mc/sec. EPR signals were recorded at 9-33 kMc/sec.

3. Results and discussion

3.1 DSC

The crystallographic phase transitions in KMnF$_3$ and TlMnCl$_3$ are known to occur at 186 K and 303 K respectively with \( c/a \) ratio in the tetragonal modification very close to unity in both. KMnF$_3$ (Minkiewicz et al. 1970) has \( c/a = 1.007 \) at 95 K and TlMnCl$_3$ (Melamud et al. 1971, Kestigian 1970) has \( c/a = 1.004 \) below 300 K. Neutron diffraction technique failed to detect these small distortions (Melamud et al. 1971). The DSC measurements are very useful in detecting and ascertaining the order of a phase transition (Karkhanavala and Rao 1971). With this view these measurements were undertaken. The DSC run on TlMnCl$_3$ is shown in figure 1 a. The strikingly excellent sensitivity of DSC to pick up the very small distortion in TlMnCl$_3$ is evident. The heat of transition \( \Delta H \) is 10 cal mole$^{-1}$. The transition appears to be first order. \( \Delta H \) obtained for KMnF$_3$ by DSG is 2 cal mole$^{-1}$. Figure 1 b shows a DSC run for KMnF$_3$ also. Earlier Deenadas et al. (1966) observed two anomalies at 83 K and 179 K (with a sample of 46.7 g) in their specific heat measurements of KMnF$_3$. The lower temperature peak, corresponding to the magnetic transition, was relatively sharp while the high temperature anomaly, attributed to the crystallographic phase transition, was about 20 K wide. This indicates that the crystallographic phase transition is second order. More recently Hirakawa and Furukawa (1970) measured the specific heat (on arbitrary scale) of KMnF$_3$ (2 g sample) with a sensitive calorimeter in the neighbourhood of the crystallographic transition. They obtained a very sharp (total span 0.5 K) anomaly at 186.6 K with a small but finite temperature hysteresis confirming it to be a first order transition. Our results on 80 mg sample of KMnF$_3$ are in agreement with this observation. The value of the transition temperature \( T_t \) obtained by us is 184 K. We could not check

![Figure 1. DSC Scans of (a) TlMnCl$_3$ (132 mg) and (b) KMnF$_3$ (80 mg) (\textcopyright R Vijayaraghavan, M D Karkhanavala, S D Damle, L C Gupta and U R K Rao 2023)]](image-url)